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Structure Determination of Gas-Phase Niobium and Tantalum Carbide Nanocrystals via Infrared Spectroscopy

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Niobium and tantalum carbide clusters have been isolated in the gas phase and irradiated with intense tunable infrared (IR) light. Stable neutral clusters are selectively ionized and subsequently detected in a mass spectrometer. By tuning the IR frequency, infrared multiphoton absorption spectra are obtained for a whole range of clusters. These mass-selective IR spectra lead to insights into the structures of small niobium and tantalum carbide clusters and nanocrystals.

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Gas-phase metal carbide clusters appear in a variety of stoichiometries and with different structures. Most of the knowledge on their structures and building principles has been obtained from the analysis of mass spectral abundance patterns. Proposed structures range from the cage-like met-car structure for the unique M4C12 stoichiometry to cubic lattice structures, which are suggested to be similar to the bulk structures of carbides [1–5]. To get more direct information on the structure of metal carbide clusters, different experimental methods have been applied, such as photofragmentation [3,6], photoionization in combination with quantum chemical calculations [7–9], or gas-phase ion chromatography [10,11]. Reactions with chlorine, oxygen, carbon monoxide, and various organic molecules can be used to probe the coordination of the “surface” atoms of the clusters [12–14]. Recently, we reported the application of the infrared resonance enhanced multiphoton ionization (IR-REMPI) technique to obtain vibrational spectra of the titanium met-car Ti8C12 [15] as well as of small titanium and vanadium carbide nanocrystals starting with the M14C13 stoichiometry [16,17].

For niobium carbide clusters, it has been shown previously that the relative abundance of the different cluster types, either met-car or nanocrystalline structures, is very sensitive to the formation conditions [3,18]. In comparison, for the carbide clusters of the heavier homologue of niobium, tantalum, it has been suggested that the cubic structures are preferred [4]. Recently, small tantalum carbide clusters up to Ta6C7 have been investigated by Heaven et al. [9] using multiphoton ionization. On the basis of accompanying density functional theory (DFT) calculations for Ta4C4, a distorted cubic shape with C2v symmetry is proposed [9], while for Nb4C4 a nearly perfect cube with Td symmetry is predicted by Harris et al. [19]. In contrast to these calculations, the reaction of Nb3C3 with O2 results in loss of two carbon atoms, which led to the proposal of a cubic structure containing Nb2 and C2 units instead of an alternating Nb and C atoms order [13].

In this study, we focus on the experimental determination of the building principles of gas-phase niobium and tantalum carbide clusters using infrared spectroscopy.
The ionization process is determined by the anharmonicity of the mode, which is important. The efficiency of the multiphoton absorption process is influenced by the value of the IP relative to the cluster’s fragmentation energy. According to recent calculations carried out by Harris et al. [19], Nb$_{14}$C$_{13}$ has a rather low ionization potential of 3.9 eV, while the binding energy per atom ($D_0$) exceeds 6 eV.

For titanium and vanadium, the smallest nanocrystalline cluster observed using IR-REMPI is (14, 13). Surprisingly, peaks corresponding to masses lower than that of (14, 13) are observed in the case of niobium carbide. The lowest peak observed corresponds to Nb$_4$C$_4$. Looking at ions that are emitted from a cluster source, Nb$_{14}$C$_{13}^+$ has been identified previously and is suggested to be the smallest (2 $\times$ 2 $\times$ 2) cubic crystal [3]. Exchanging one carbon atom for a niobium atom results in Nb$_5$C$_3$.

By tuning FELIX’s wavelength while monitoring the mass selected ion yield, the infrared spectra of the clusters can be obtained. In the present experiment, FELIX is tuned from 370 to 1650 cm$^{-1}$, and the infrared spectra of all stable clusters shown in Fig. 1 are measured simultaneously. In Fig. 2 the infrared spectra of selected masses are shown. Above 760 cm$^{-1}$, the ion yield is low and shows no clear wavelength dependence. A single broad resonance is observed for the smallest two clusters, (4, 4) and (5, 3) with the maxima at 675 and 660 cm$^{-1}$, respectively. A new peak is observed for the (9, 9) cluster at 520 cm$^{-1}$. Its position shifts continuously from 505 cm$^{-1}$ for (14, 13) to 480 cm$^{-1}$ for (50, 50). The infrared spectra of Nb$_{14}$C$_{13}$ and the larger clusters are very similar. The two modes are observed for up to at least (32, 32). However, the mode around 650 cm$^{-1}$ becomes very low in relative intensity.

The mass distribution of ionized tantalum carbide clusters, obtained by IR multiphoton ionization averaged over
the 400–770 cm\(^{-1}\) range, is shown in Fig. 3. The cluster distribution is similar to the one observed for niobium carbide with the maximum corresponding to the (4,4) cluster and intensity drops behind the signals assigned to the (14,13), (18,18), and (24,24) clusters, which are again consistent with geometrical shell closings of cubic nanocrystals. Infrared spectra of tantalum carbide clusters are presented in Fig. 4. The spectra exhibit two cubic nanocrystals. Infrared spectra of tantalum carbide to the \(/H_2O\) \(^{849}\) cluster and intensity drops behind the signals assigned carbide with the maximum corresponding to the \(670\) second around \(675\), and \(480\) towards \(670\) and Dance [19]. For the Nb \(4\) niobium carbide clusters have been calculated by Harris for the bulk phase. Recently, vibrational spectra of small clusters in our experiment have a different structure than predicted on the basis of the DFT calculations. An alternative Nb\(_4\)C\(_4\) isomer has been suggested by Deng et al. [13], in which C\(_2\) units are present. From the infrared spectra shown here, there is no evidence for the presence of such an isomer. If it contains C=C units as in the met-cars, a strong signal would be expected in the C=C stretch region. For met-cars, this vibration corresponds to intense absorption in the 1200–1400 cm\(^{-1}\) range, e.g., for Ti\(_8\)C\(_{12}\) at 1395 cm\(^{-1}\) [15]. Since none of the presented clusters shows IR active modes higher than 800 cm\(^{-1}\), that contradicts the proposed existence of C\(_2\) units in the cluster structures, but supports the presence of isolated C atoms.

Both niobium as well as tantalum carbide are metallic in the solid. Their IR spectral properties are thus difficult to determine. However, electron energy loss spectroscopy (EELS) gives information on optically active (surface) phonon modes of these materials. In Fig. 2 we show also the positions of the EELS bands of the (100) surface of fcc NbC [21]. Two IR active bands have been identified, centered at 490 and 635 cm\(^{-1}\). For fcc TaC (see Fig. 4), the position of the EELS peaks for the (100) surface are slightly shifted in comparison to NbC to 465 and 660 cm\(^{-1}\), respectively [21].

Considering the enormous difference in dimensions and phase, the agreement between the gas-phase spectra of small niobium and tantalum carbide nanocrystals and the EELS spectrum of the bulk material with the fcc structure is striking. Although the infrared modes observed

![FIG. 3. Mass distribution of Ta\(_x\)Cy clusters formed via thermionic emission. The mass spectrum has been integrated while FELIX is tuned through the 400–770 cm\(^{-1}\) region.](image3)

![FIG. 4. Infrared multiphoton absorption spectra of selected Ta\(_x\)Cy clusters. The frequencies of optical active EELS bands of the TaC (100) surface are marked by the dashed lines [21].](image4)
experimentally are undoubtedly envelopes of a set of modes, detailed analysis of the data can unravel some basic properties about the nature of these modes.

Characteristic surface-localized optical modes of rock-salt structured crystals were found previously by Wallis et al. [23] and by Lucas [24] for NaCl (100). The “Wallis” mode is associated with out-of-plane vibrations (i.e., perpendicular to the surface), and the “Lucas” mode with in-plane vibrations (i.e., parallel to the surface). Similarly, Oshima et al. [21] assigned the modes in their EELS spectra as the motion of the light carbon atom parallel (higher frequency) or perpendicular (lower frequency) to the surface. Obviously, it is difficult to transfer such concepts to small clusters, where most atoms are located on corner or edge positions. Nonetheless, it is striking to see how the low frequency mode is negligible or not present at all for small clusters, but starts growing for the (9, 9) cluster and becomes the dominant mode for clusters larger than (14, 13). This trend is accompanied by an increasing mean coordination number of the carbon (and the metal) atoms.

The sudden growth of the low frequency band at about 500 cm$^{-1}$ is connected with the transition from a two-layered to a three-layered structure between the $2 \times 3 \times 3$ (9, 9) and the $3 \times 3 \times 3$ (14, 13) clusters. This structure-related change of the IR spectrum allows one to analyze the geometry of intermediate clusters. For example, since the spectrum of the (12, 12) cluster resembles the spectrum of the (14, 13) rather than that of the (9, 9) cluster, it is most likely that its structure is not the $2 \times 3 \times 4$ cuboid but a defective (14, 13) cube, missing one carbon and two metal atoms (possibly one row on an edge of the cube). In general, both components, the metal and the carbon atoms, prefer a filled coordination sphere. Therefore, the defective cube structure should be preferred, because of the higher mean coordination number in comparison to the flat $2 \times 3 \times 4$ cluster. Based on the (14, 13) cube, its defect structures may also contain a central carbon atom coordinated by six metal atoms. Possibly, the appearance of the 500 cm$^{-1}$ band is connected to this structural element. In an analogous way, the spectral properties of the (10, 11) cluster suggest its existence in the form of a $3 \times 3 \times 3$ cube with two missing edge rows. In these cases, the IR spectra directly indicate which types of isomers are preferred in the growth mechanism of metal carbide nanocrystals.

The results shown here demonstrate the potential that infrared spectroscopy of gas-phase clusters has when combined with mass selectivity. The patterns observed in the thermionic emission mass spectra of niobium and tantalum carbide clusters indicate geometric shell closings of cubic nanocrystals. Consistent with this, large clusters show IR spectra in which the optical surface phonons of the bulk can be clearly recognized. A clear break can be observed around M$_4$C$_{11}$, as smaller clusters have pronouncedly different IR spectra. These differences might be attribut- able to a transition from a two-layered ($2 \times 3 \times 3$) to a three-layered ($3 \times 3 \times 3$) cluster structure. More elaborate theoretical calculations are needed to clarify this. The recent structural identification of Ti$_4$C$_2$ [25] showed that experimental IR spectra of gas-phase clusters are a fruitful basis for such calculations.

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